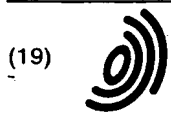


(11)



Europäisches Patentamt
European Patent Office
Office européen des brevets



(11) **EP 1 074 607 A1**

(12)

EUROPEAN PATENT APPLICATION

(43) Date of publication:

07.02.2001 Bulletin 2001/06

(51) Int. Cl.⁷: **C11D 3/395, C11D 3/37,
C11D 3/39**

(21) Application number: **00116077.9**

(22) Date of filing: **27.07.2000**

(84) Designated Contracting States:

**AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU
MC NL PT SE**

Designated Extension States:

AL LT LV MK RO SI

(30) Priority: **04.08.1999 IT MI991757**

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(54) **Water based dispersions of percarboxylic acids**

(57) Water-based dispersions of the ϵ -phthalimido peroxyhexanoic acid comprising as stabilizers copolymers of methyl-vinyl-ether with the acid and/or maleic anhydride, in 1:1 ratio with alternated structure, usable in detergent, hygienizing, cosmetic applications.

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Description

[0001] The present invention relates to water dispersions of percarboxylic acids in crystalline form usable in detergent and/or hygienizing, cosmetic systems. More specifically water dispersions of crystals of ϵ -phthalimido peroxyhexanoic acid, herein called PAP, having a high chemical stability and an improved physical stability, usable in detergent and hygienizing systems stable during the time for at least 6 months.

[0002] Organic peroxyacids are well known for their efficacy as bleaching and hygienizing agents also at low temperatures. To this class of compounds belong peroxydicarboxylic acids solid at room temperature usable in formulations in powder or in tablets typical of the detergency.

[0003] Among peroxydicarboxylic acids of particular interest the ϵ -phthalimido peroxyhexanoic acid is very effective as bleaching, hygienizing and deodorizing agents, and in general as oxidizer, already under mild conditions of temperature and pH. The ϵ -phthalimido peroxyhexanoic acid is suitable for the preparation of formulations for use in the detergent and cosmetic industry, since it has an exceptional thermal and at storage stability as well as a particularly favourable toxicological and ecotoxicological profile.

[0004] It is besides well known for the applications in the detergency and hygienizing field the use of liquid systems having an aqueous basis containing active principles not dangerous either for men or for the environment, having a sufficient chemical and physical stability such as to be used in consumer goods, for the distribution and exposure to the public for even long periods of time. For these systems an high chemical stability and an improved physical stability are required, in environmental temperature conditions from 15° to 35°C for at least 6 months.

[0005] In the case of organic peroxyacids to be used as active principles for said liquid systems in the detergency and hygienizing field, it is difficult to formulate water-based systems with the above mentioned chemical physical stability properties.

[0006] In particular in the case of solid peroxyacids as the mentioned ϵ -phthalimido peroxyhexanoic acid, the formulations having a water basis are heterogeneous systems, wherein the peracid crystals are dispersed in a continuous water phase.

[0007] It is known from the technology of the production of the ϵ -phthalimido peroxyhexanoic acid to obtain dispersions of crystals of said acid in water mediums (slurry), characterized by a satisfactory chemical stability of the acid itself but by a low physical stability: in fact said slurries show, in absence of stirring, segregation and sedimentation also in short times. This means that these industrially useful products are difficult to be used as consumer goods due to their insufficient physical stability, since as known, for this application the products must be stable upon storage without stirring for at least 6 months.

[0008] It is known in the prior art the use of chemical auxiliary agents having properties of thickening and viscosity improver agents to be introduced in the water-based crystal dispersions to improve the physical stability thereof. But even though numerous auxiliary compounds are known, able to stabilize water-based dispersions of crystals of chemical compounds having relatively low reactivity, in the case of the ϵ -phthalimido peroxyhexanoic acid, its high chemical reactivity makes it impossible to produce a water-based system having a high chemical stability and improved physical stability lasting during the time.

[0009] The need was therefore felt to identify auxiliary agents suitable to develop water-based systems containing crystals of ϵ -phthalimido peroxyhexanoic acid in the form of dispersions having a high chemical stability and improved physical stability during the time.

[0010] The Applicant has surprisingly and unexpectedly found auxiliary agents suitable for the preparation of chemically and physically stable water based dispersions of the ϵ -phthalimido peroxyhexanoic acid.

[0011] An object of the present invention are water-based dispersions of the ϵ -phthalimido peroxyhexanoic acid comprising as stabilizers copolymers of methyl-vinyl-ether with the acid and/or the maleic anhydride, in 1:1 ratio having an alternate structure.

[0012] Said polymers generally have a weight average molecular weight in the range 200,000-2,000,000.

[0013] Such stabilizers are in the market as, e.g., GANTREZ^R by ISP.

[0014] The amount of PAP can range between 1-30% by weight, preferably between 3-20% by weight.

[0015] The amount of the stabilizers (auxiliary agents) of the invention generally varies in the range 0.2-5% by weight, preferably 1.5-4% by weight, still more preferably 2-4%.

[0016] The organic peroxyacid PAP is well known in the prior art for uses in the detergency and hygienizing field and also for its use in bleach, see EP 325,289 herein incorporated by reference.

[0017] The organic peroxyacid PAP contained in the suspensions (dispersions) of the present invention is under the form of crystalline particles having sizes generally in the range 5-200 micron, as determinable by optical microscope.

[0018] In the water-based dispersions of the ϵ -phthalimido peroxyhexanoic acid of the present invention additional components such as polymers of natural origin of polysaccharide type, preferably selected from guar rubber and xanthan rubber, products described, for example in Merck Index, edition XII, number 4,602 of page 780 and number 10,191 of page 1,718, respectively, can optionally be present. In the suspension said optional stabilizers are in the range 0.1%-

1.5% by weight.

[0019] The total amount of stabilizers contained in the dispersion is in the range 0.2-5% by weight, preferably 1.5-4% by weight, still more preferably 2-4%.

[0020] Other optional components which can be added having the function to stop the catalytic action of heavy metal ions on the decomposition of the peroxyacid, are chelants and/or sequestrants in amounts from 0.005 to 5% by weight. Quinoline and its salts, alkaline metal polyphosphates, picolinic and dipicolinic acid, mono- or polyphosphonic acids, for example preferably the 1-hydroxyethylidene-1,1-diphosphonic acid (HEDP) can be mentioned.

[0021] The physical stability in the time, at room temperature, of the dispersions of the present invention (see for example Table 1) can be visually checked by ascertaining the unmixing presence or absence after six months. More suitably it can be checked that in the period of two months no unmixing appears and that the dispersion viscosity, generally in the range 500-2,000 centipoise, does not change in absolute value more than 10%, preferably 7%, when a copolymer of methylvinylether with maleic acid is used in 1:1 ratio having a weight average molecular weight 1,900,000. With said viscosity variations, the Applicant has found that the dispersion remains physically stable for at least six months.

[0022] The chemical stability during the time, at room temperature, of the dispersions of the present invention is determined by the active oxygen content, determined by iodometric titration and expressed in %, the 100% being defined the content of active oxygen at the beginning of the storage.

[0023] The viscosity of the PAP water-based dispersions according to the present invention, expressed in centipoise (cPs), is measured by Brookfield viscometer at 25°C with rotary probe at 60 rpm.

[0024] The following examples are given for illustrative but not limitative purposes of the present invention.

EXAMPLE 1

[0025] 25 g of alternated copolymer methylvinylether-maleic acid, having molecular weight 1.9×10^6 , are slowly added to 385 g of distilled water. Stirring is maintained for 20 minutes until complete dissolution of the polymer.

[0026] 170 g of ϵ -phthalimido peroxyhexanoic acid in powder are separately dispersed in 400 g of distilled water.

[0027] The two above described liquids are mixed together and kept under stirring for 20 minutes; a creamy liquid having a Brookfield viscosity of 830 cPs is obtained. The physical and chemical stability data during the time are reported respectively in Tables 1 and 2.

EXAMPLE 2

[0028] 10 g of alternated copolymer methylvinylether-maleic acid, having molecular weight 1.9×10^6 , are slowly added to 385 g of distilled water. Stirring is maintained for 20 minutes until complete dissolution of the polymer.

[0029] 170 g of ϵ -phthalimido peroxyhexanoic acid in powder and 10 g of Guar rubber are separately dispersed in 400 g of distilled water.

[0030] The two above described liquids are mixed together and kept under stirring for 20 minutes; a creamy liquid having a Brookfield viscosity of 980 cPs is obtained. The physical and chemical stability data during the time are reported respectively in Tables 1 and 2.

EXAMPLE 3

[0031] 10 g of alternated copolymer methylvinylether-maleic acid, having molecular weight 1.9×10^6 , are slowly added to 385 g of distilled water. Stirring is maintained for 20 minutes until complete dissolution of the polymer.

[0032] 170 g of ϵ -phthalimido peroxyhexanoic acid in powder and 3 g of Xanthan rubber are separately dispersed in 432 g of distilled water.

[0033] The two above described liquids are mixed together and kept under stirring for 20 minutes; a creamy liquid having a Brookfield viscosity of 910 cPs is obtained. The physical and chemical stability data during the time are reported respectively in Tables 1 and 2.

EXAMPLE 4 comparative (comp)

[0034] 5 g of acrylic-sodiumacrylate-acrylamide acid copolymer, having molecular weight 5×10^6 , commercialized as ECOCLAR® by AUSIMONT, are solubilized in 825 g of distilled water.

[0035] A solution at pH 7, having a Brookfield viscosity of 960 cPs is obtained.

[0036] In such solution 170 g of ϵ -phthalimido peroxyhexanoic acid in powder are dispersed under mild stirring; a suspension having a Brookfield viscosity of 1,100 cPs is obtained. The physical and chemical stability data during the time are reported respectively in Tables 1 and 2. The chemical instability of the suspension is evident, wherefore the

product has no interest from the application point of view.

EXAMPLE 5 comparative (comp)

- 5 [0037] 170 g of ϵ -phthalimido peroxyhexanoic acid in powder are dispersed in 817 g of distilled water. 10 g of Guar rubber and 3 g of Xanthan rubber are added under stirring. The obtained mixture is subjected to stirring for 20 minutes until dissolution of the stabilizers; a suspension having a Brookfield viscosity of 1,100 cPs is obtained. The physical and chemical stability data during the time are reported respectively in Tables 1 and 2.

Table 1

Examples	physical stability in the time at room temperature		
	48 hours	8 weeks	24 weeks
1	not unmixed viscosity 830cPs	not unmixed viscosity 810cPs	not unmixed viscosity 780cPs
2	not unmixed viscosity 950cPs	not unmixed viscosity 900cPs	not unmixed viscosity 840cPs
3	not unmixed viscosity 890cPs	not unmixed viscosity 850cPs	not unmixed viscosity 800cPs
4(comp)	not unmixed	--	--
5(comp)	unmixed	--	--

Table 2

Examples	chemical stability in the time at room temperature		
	48 hours	8 weeks	24 weeks
1	99.7%	99.2%	98.1
2	99.5%	98.5%	97.2%
3	99.3%	98.9%	98.0%
4(comp)	71.0%	--	--
5(comp)	99.2%	--	--

[0038] From the data reported in the Tables it can be noticed that physically stable water-based systems (Example 4 comp) containing in suspension fine crystals of the PAP peracid have not the necessary chemical stability, decreasing in quality due to the active principle decay, with loss of peroxidic oxygen.

[0039] Viceversa it happens that chemically stable water-based systems (Example 5 comp) containing in suspension fine crystals of the PAP peracid, have not the necessary physical stability, with loss of uniformity and decomposition in differentiated phases also just after the preparation.

Claims

1. Water-based dispersions of the ϵ -phthalimido peroxyhexanoic acid comprising as stabilizers copolymers of methyl-vinyl-ether with the acid and/or maleic anhydride, in 1:1 ratio having an alternate structure.
2. Dispersions according to claim 1, wherein the weight average molecular weight is in the range 200,000-2,000,000.
3. Dispersions according to claims 1-2, wherein the amount of ϵ -phthalimido peroxyhexanoic acid ranges between 1-30% by weight, preferably between 3-20% by weight.
4. Dispersions according to claims 1-3, wherein the stabilizer amount ranges from 0.2-5% by weight, preferably 1.5-

4% by weight, still more preferably 2-4%.

5. Dispersions according to claims 1-4, wherein additional components such as polymers of natural origin of polysaccharide type are present.

6. Dispersions according to claim 5, wherein the polysaccharides are selected from guar rubber and xanthan rubber.

7. Dispersions according to claims 5-6, wherein the polysaccharides are in the range 0.1%-1.5% by weight.

8. Dispersions according to claims 1-7, wherein components having the function to stop the catalytic action of heavy metal ions on the decomposition of the peroxyacid are present, in an amount from 0.005 to 5% by weight, selected from chelants and/or sequestrants.

9. Dispersions according to claim 8, wherein said components are selected from one or more of the following: quino-
line and its salts, alkaline metal polyphosphates, picolinic and dipicolinic acid, mono- or poly phosphonic acids, preferably the 1-hydroxyethylidene-1,1-diphosphonic acid (HEDP).

10. Use of the dispersions according to claims 1-9 in detergent, hygienizing, cosmetic applications.



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EUROPEAN SEARCH REPORT

Application Number
EP 00 11 6077

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
X	US 5 073 285 A (LIBERATI PATRICIA ET AL) 17 December 1991 (1991-12-17) * column 3, line 35 - column 4, line 10 * * column 12, line 22 - line 30 * * claim 1 * ---	1-4,8-10	C11D3/395 C11D3/37 C11D3/39
X	US 4 992 194 A (LIBERATI PATRICIA ET AL) 12 February 1991 (1991-02-12) * column 3, line 48 - column 4, line 7 * * column 12, line 20 - line 28 * * claims 1-9 * ---	1-4,8-10	
P,X	WO 00 27960 A (BUZZACCARINI FRANCESCO DE ;DRESCO PIERRE ANTOINE (FR); SCIALLA STE) 18 May 2000 (2000-05-18) * page 15, line 24 - page 16, line 29 * * examples I-IV * * claims 1-13 * ---	1-10	
P,A	EP 1 010 751 A (PROCTER & GAMBLE) 21 June 2000 (2000-06-21) * page 8, line 30 - line 51 * * page 9, line 46 - line 48 * ---	1-10	TECHNICAL FIELDS SEARCHED (Int.Cl.7)
A	EP 0 890 635 A (MANITOBA ITALIA SPA) 13 January 1999 (1999-01-13) * page 2, line 58 - page 3, line 45 * ---	1-4,8,10	C11D A61K
A	EP 0 763 595 A (UNILEVER NV ;UNILEVER PLC (GB)) 19 March 1997 (1997-03-19) * page 6, line 23 - line 36 * * page 7, line 4 - line 37 * ---	1-5,8-10	
A	EP 0 852 259 A (AUSIMONT SPA) 8 July 1998 (1998-07-08) * page 3, column 3, line 32 - line 40 * * claim 1 * -----	1,9	
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 13 October 2000	Examiner Richards, M
CATEGORY OF CITED DOCUMENTS X: particularly relevant if taken alone Y: particularly relevant if combined with another document of the same category A: technological background O: non-written disclosure P: intermediate document T: theory or principle underlying the invention E: earlier patent document, but published on, or after the filing date D: document cited in the application L: document cited for other reasons &: member of the same patent family, corresponding document			

EPO FORM 1503 (03.02.92) (P/4C311)

**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 00 11 6077

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on
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13-10-2000

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 5073285 A	17-12-1991	US 4992194 A	12-02-1991
		CA 2056365 A,C	13-12-1990
		DE 69001249 D	06-05-1993
		DE 69001249 T	12-08-1993
		WO 9015857 A	27-12-1990
		EP 0477190 A	01-04-1992
		ES 2054354 T	01-08-1994
US 4992194 A	12-02-1991	CA 2056365 A,C	13-12-1990
		DE 69001249 D	06-05-1993
		DE 69001249 T	12-08-1993
		WO 9015857 A	27-12-1990
		EP 0477190 A	01-04-1992
		ES 2054354 T	01-08-1994
		US 5073285 A	17-12-1991
WO 0027960 A	18-05-2000	WO 0029536 A	25-05-2000
		AU 1521999 A	05-06-2000
		AU 1615800 A	29-05-2000
EP 1010751 A	21-06-2000	EP 1010750 A	21-06-2000
		AU 1938200 A	03-07-2000
		WO 0036072 A	22-06-2000
EP 0890635 A	13-01-1999	IT MI971617 A	08-01-1999
EP 0763595 A	19-03-1997	US 5633223 A	27-05-1997
		CA 2183125 A	01-03-1997
EP 0852259 A	08-07-1998	IT MI970005 A	03-07-1998
		BR 9706511 A	18-05-1999
		JP 10195484 A	28-07-1998
		US 6080715 A	27-06-2000

EPO FORM P0459

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82